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Nanocalorimetry

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1. Definition

Calorimetry is the part of thermodynamics which aims to measure any quantity of heat (enthalpy, specific heat, heat release) stored, released or brought into play in any state of matter, in a reaction, or in phase transitions [Lavoisier1780].

More precisely, the terminology of “Nanocalorimetry” may cover different concepts depending on the area of science where it is used. It concerns any calorimetric method in which either the samples to be studied have a size in the range of the nanometer scale or the measured energies involved are of the order of the nanojoule or below.

Although these two types of definitions are very different, they both have something in common. They are indeed concerned by the development of miniaturized sensors and more generally by ultrasensitive experiments imposed when small systems are involved. Indeed most of the modern sensors are built to carry out measurements at the ultimate limit of what can be detected by calorimetry on thin films or very small volume samples.

In this article, the key issues governing an experiment of nanocalorimetry is discussed. In particular, for each point, recent experiments conducted in this area over the world are presented. This will provide a non-exhaustive overview of what is currently done in nanocalorimetry. Particular attention will be given to micro and nanofabrication technologies as well as highly sensitive thermal technique necessary to achieve an experiment of nanocalorimetry. Here bolometry is not discussed, despite its thematic proximity; the measurement of radiation and possible refrigeration at the mesoscopic scale has been described extensively in other works [Giazotto2006].

2. Nanocalorimetry

2.1 Introduction

In calorimetry, thermal isolation is the major issue. The heat capacity of a sample under study, or the measurement of exchanges of energy between the sample and its environment, is properly measured only if the sample is correctly isolated from its environment (adiabatic conditions). In practice, the thermal isolation is not perfect, and one overcomes this problem by calibrating correctly the thermal link between the sample and its surroundings. As discussed later in this article, the thermal relaxation rate, τ , which determines the condition of adiabaticity, is a crucial parameter for the selection of measurement methods adapted to the physics to be studied (see the section Experimental techniques). This problem of thermal isolation is more problematic in nanocalorimetry because the samples are very small in size and therefore have small masses and thus very small heat capacities. Therefore, to fulfill the requirement of adiabaticity, the experimentalist makes thin suspended membranes micrometer thick that will support small objects to be studied (see Fig. 1).

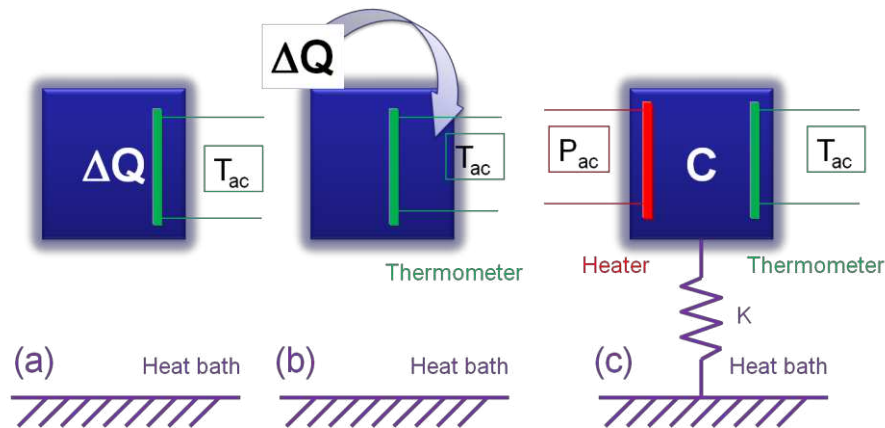


Figure 1 Thermal schemes for calorimetric experiments (a) a quantity of heat ΔQ is released in the sample, an increase of temperature will appear. This system is assumed to be infinitely isolated from the heat bath. (b) An external heat is supplied to the sample also infinitely isolated from the heat bath. By measuring the increase of temperature we will get access to the heat capacity of the sample (adiabatic calorimetry). (c) The sample is link to the heat bath through a thermal conductance K , a thermometer and a heater will allow the measurement of the thermal properties (C and K).

One of the advantage of working with membrane sensor is the reduction of addenda (the sample holder and the sensitive measuring elements are called "addenda"); this is especially important when working with very small systems. The small thickness of the membrane reduces also the thermal coupling to the outside providing then thermal isolation. Some membranes are structured to further limit the exchange of heat between the measurement area and the thermal bath. In this case, they look like micro-trampolines suspended by arms that allow the passage of current leads (see Fig. 2).

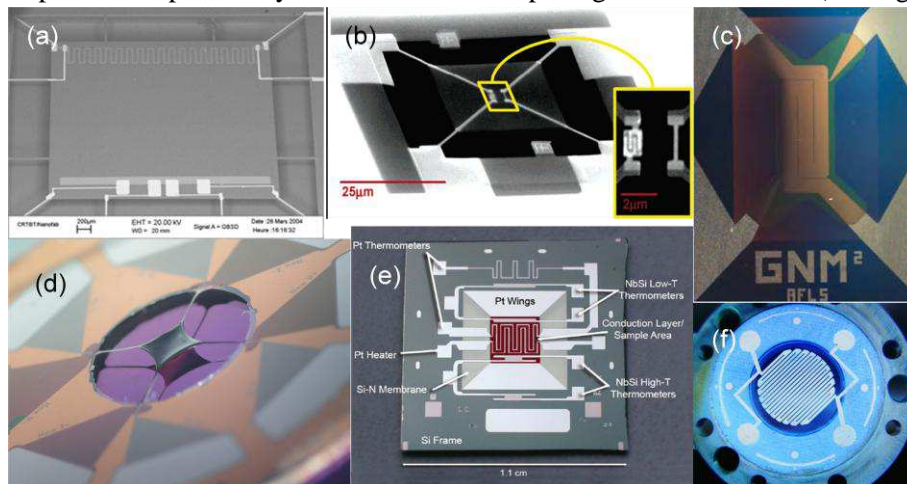


Figure 2 Various sensors made in silicon, silicon nitride or polymer. a) Silicon membrane for very low temperature heat capacity measurement by ac calorimetry [Bourgeois2005] b) silicon nitride sensor made by ebeam lithography used for relaxation calorimetry [Chung2005] c) Silicon nitride sensor used for fast scanning calorimetry [Lopeandia2008] d) Polyparaxylylene membrane for phase transition detection in thin magnetic films around 100K [Lopeandia2010] e) silicon nitride sensor used for relaxation calorimetry over a wide range of temperature [Cooke2010] f) Polyimide membrane for heat capacity measurement of thin polymer films at ambient temperature [Garden2009].

Another point is that since in the case of nanocalorimetry the amount of energy to be measured is small, the resolution of the calorimetric measurement must be sufficiently high to access the expected thermal properties. A first means to increase the signal to noise ratio (SNR) of the measurement is to reduce the noise of the detected signals. In other words, one must develop a low noise electronic chain adapted to the chosen experimental technique and also adapted to the sensor converting temperature

changes in measurable signals (usually voltage). This aspect, which concerns the sensitive measurements and thermometry, is discussed later on (see the section "Thermometry"). A second way is to reduce significantly the heat capacity of sample holder and measuring devices (thermometers and heaters).

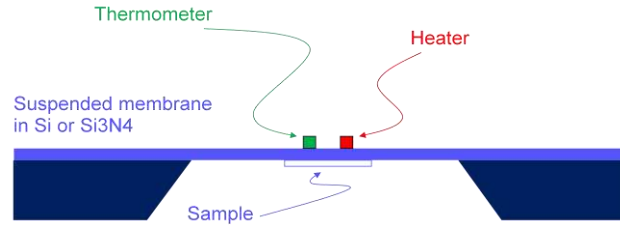


Figure 3 Scheme of the principle of a nanocalorimetric measurement on membrane.

In this case, the use of nanotechnology and microfabrication is indispensable for the realization of sample holder for which the heat capacity is at least equivalent (or smaller) than the sample heat capacity being studied. The use of these technologies is crucial for measuring heat capacities of objects of very small size or for the detection of low energy in relevant thermodynamic transformations. Therefore, micro and nanotechnologies are essential keys to nanocalorimetry. This justifies the use of thin microfabricated membranes for thermal isolation (see figure 3). Each membrane contains the sensitive elements. These elements are micro-machined in thin layers of sub-micrometer thicknesses deposited by vacuum evaporation technique or by magnetron sputtering. Microphotolithography techniques are used to shape the geometry of the sensitive elements and define their impedances, and therefore define the sensitivity of the calorimetric measurement.

Another major issue in calorimetry is the temperature homogeneity of the sample and the addenda. Indeed, the low thermal diffusivity of some samples limits the dynamic of temperature variations during the measurement. The relaxation time of thermal diffusion in the sample and addenda, τ_{diff} , also depends on the geometry of nanocalorimeters. In general, a thin layer of gold, or highly diffusive material, is deposited by vacuum evaporation technique or sputtering on the measurement area so that the temperature is as uniform as possible in the sample. Finally, the thin thickness of the membranes reduces the thermal coupling to the outside providing then thermal isolation, while the isothermal layer ensures thermal homogeneity of the sensitive area. The experimental time scale Δt_{exp} , the time scale over which the thermal measurement occurs has to be slower than the diffusion time (to ensure a homogeneous temperature) and faster than the thermalization time of the sensing part to the heat bath. This last point can be mathematically summarized by the two following inequalities:

$$\tau_{\text{diff}} \ll \Delta t_{\text{exp}} \ll \tau$$

where τ_{diff} is the thermal diffusion time and τ is the thermal relaxation time.

2.2 Thermometry

The basis of the measurement of heat is essentially based on the ability of the experimentalist to accurately measure temperature. To obtain a sensitive measurement of temperature, it requires access to a physical quantity X , which varies greatly with temperature. This large variation with temperature is characterized by what is called the temperature coefficient $\frac{1}{X} \frac{dX}{dT}$. A highly sensitive measurement of temperature variation will allow a direct access to very small energy, which is the case generally when nanosystems are involved. The physical quantity X will be anything that can be accurately measured : a volume, a pressure or an electrical quantity (capacitance, resistance etc...).

Some of the most used technique to measure temperature in nanocalorimetric experiments are detailed below.

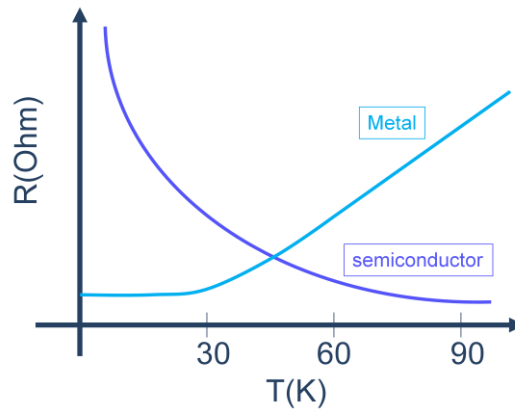


Figure 4 Variation of resistance versus temperature in the cases of metals and semiconductors.

Resistive thermometry: one of the most commonly used physical quantities to measure a temperature is the resistance. The resistivity of pure metals is changing a lot with temperature from very high temperature down to 30K. Then these metals will be perfect thermometers in this temperature range. The most common thermometer is platinum; this metal when elaborated in thin films geometry has a positive temperature coefficient of resistance of about $\frac{1}{R} \frac{dR}{dT} = 3 \times 10^{-3} \text{K}^{-1}$; the resistance is decreasing when the temperature is decreased. Other materials have also a strong change of resistance with temperature like semiconductor or like Anderson or Mott insulator. These materials have a huge increase of resistance as the temperature is lowered because the electron transport is more and more limited as the thermal activation is diminished. These materials (germanium, carbon, niobium silicon, niobium nitride) are widely used as thermometer at low temperature. They are much more efficient than metals below 40K with temperature coefficient that can be above 1 K^{-1} ! Temperatures as low as few millikelvin, close to the absolute zero, may be measured using this type of thermometry. The limitation comes from the applied current necessary to measure the resistance; the Joule heating creates parasitic power. This dissipated power may induce temperature gradients and then induces error when estimating the real temperature of a nanosystem.

Noise thermometry: any electrons in a regular resistance are subject to brownian motion. This brownian motion takes its origin in the temperature activation. This movement of electrons gives birth to a varying voltage across the resistor which is called the Johnson-Nyquist noise. Due to its origin this noise is a function of the temperature through $V = \sqrt{4k_B T R \Delta f}$, where k_B is the Boltzmann constant, T the temperature, R the resistance and Δf the frequency window where this noise is measured. By measuring the voltage versus time, knowing the resistance, one can deduce the temperature of the resistor R . This thermometry is not very sensitive but it has the major advantage of not dissipating any spurious power because its measurement does not require any electrical current.

Thermocouple thermometry. A thermocouple is composed by a junction between two different materials. A temperature difference between a "hot" and a "cold" junctions will be converted into a voltage (Seebeck effect). The measurement of this voltage is widespread way of measuring a temperature. However, the amplitude in volt per Kelvin produced by a usual thermocouple is small (of the order of magnitude of several hundreds of microvolts per degree), it needs at least a few hundred couples in a system called thermopile to obtain sensitivities equivalent to those of resistive thermometers.

A thermopile is a device composed of plenty of thermocouples connected electrically in series and thermally in parallel. Each couple participates in the total impedance of the sensor and therefore increases the thermal noise of electrons in conductors (Johnson-Nyquist noise). The fact that it is not necessary to polarize and thus generate thermal power in the sample to obtain a measuring signal is a major advantage of this technique.

When working close to room temperature, most calorimeters and differential nanocalorimeters use thermopile to measure directly the temperature difference between the sample cell and a reference neutral cell (see DSC). In this case, the "hot" and "cold" junctions are perfectly thermally coupled to the sample and reference respectively (or vice versa). For zero signal detection devices, two thermopiles connecting sample/thermal-bath and reference/thermal-bath respectively are mounted in opposition in order that same temperature elevations of the sample and references with respect to thermal bath gives approximately zero signal. Knowing the thermal link (thermal exchange coefficient) between the sample and the reference with respect to the surrounding, the voltage from the thermopile is proportional to the difference of heat flows (W) exchanged between the sample and the reference with respect to thermal bath respectively. One prefers to present the converted signals collected by thermopiles in watts rather than in Kelvin because their direct integration along time gives the heat absorbed or released by the sample during the experiment of calorimetry. In conclusion, the thermopile is the ideal element to detect differential temperature or differential heat flow between two objects without direct generation of power in one or (and) the other of these objects.

3. Experimental techniques

3.1 Principle of measurement

Calorimetry is the measurement of heat exchanges between a system for which the thermal properties have to be studied and its environment (thermal bath). There are two types of calorimetric measurements. The first is the measurement of the specific heat. In this case, the experimentalist provides a given heat flux to the sample and measures the resulting temperature rise (Figure 1c). The second concerns the measures of energy released or absorbed by a sample during any transformations or physicochemical interaction at constant temperature; one speaks in this case about isothermal calorimetry. In all cases, the experiment of calorimetry consists in measuring a change in temperature. Thermometry and the measurement electronics are therefore two essential elements for nanocalorimetry. The temperature sensor is then chosen as a function of the particular experimental methods used; the latter being in fact adapted to the physical phenomena that the experimentalist wishes to study.

Let us introduce two characteristic times which will be very useful in the rest of this article. First the internal thermalisation time noted τ_{int} is defined; this time is related to the diffusion of heat inside the sample to be studied. Secondly, the external thermalisation time noted τ_{ext} is defined. This time is given by the ratio C/K where C is the heat capacity of the system and K the thermal conductance of the link to the bath (see Figure 1). If a heat power is supplied to the sample at a rate faster than the internal thermal time then the temperature of the sample is not homogeneous (see Figure 5). On the other hand if a power is supplied to a sample over a very long time then the external thermal time will be dominant. A gradient of temperature will be established following an exponential law between the sample and the heat bath as shown in the figure 5.

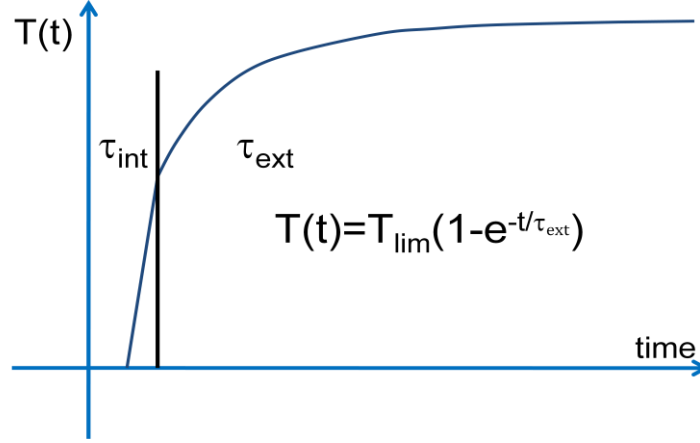


Figure 5 Illustration of the two significant time scales in a nanocalorimetric experiment.

3.2 Experimental methods

3.2.1 Adiabatic calorimetry

Regarding the specific heat, various experimental methods allow its measurement. The most traditional is the adiabatic calorimetry in which the sample and its addenda are isolated as much as possible from their environment. A thermal power of known value is sent at a time scale much smaller than the thermal relaxation time τ_{ext} . The measured temperature rise is inversely proportional to the heat capacity of the sample (plus addenda)

$$\Delta T = \frac{\int_0^{\Delta t} P dt}{C}$$

Then, it remains simply to change the temperature of the thermal bath and carry out a new measurement in order to have a final $C(T)$ curve. In practice, adiabaticity is not perfect, and the heat exchange coefficient has to be taken into account, and therefore energy losses between the sample and the thermal bath. This is especially true in nanocalorimetry because objects to be studied are small and therefore their heat capacity is small to. It is therefore very difficult to thermally isolate them, and the adiabatic nanocalorimetry method cannot be implemented. Scientists have developed calorimetric techniques better suited to the measurement of small samples to overcome the problem of heat loss. They are presented in the following.

3.2.2 Differential scanning calorimetry

A second widespread calorimetric experimental technique is called differential scanning calorimetry (DSC) [Claudy2005,Höhne2010]. It is a continuous method in which the sample temperature follows a temperature ramp imposed by the experimentalist (Figure 6). The fact that it is differential indicates that what is measured is directly the temperature difference between the sample and a neutral reference. However, one must keep in mind that any calorimetric method can be conceived in differential mode. In the case of DSC, differential heat capacity ΔC and differential heat flux ΔP (between sample and reference) measured during the ramp temperature obey to a first order the following equation:

$$\Delta C = \frac{\Delta P + \tau \frac{d(\Delta P)}{dt}}{\beta}$$

where β is the scanning temperature rate and τ the thermal relaxation time. This differential heat flux (or thermal power) is related to the differential temperature by means of the heat exchange coefficient K :

$$\Delta P = K \Delta T$$

Compared with the adiabatic calorimetry, here the heat exchange coefficient K also plays a role at the same level than the heat capacity C . The former is measured by means of a prior calibration in quasi-static mode where the above equation is valid. In DSC, the scanning rate $\beta = dT / dt$, is an important factor since it determines the signal intensity. Indeed, the first equation above shows that for a given differential heat capacity, the differential signal ΔP is for a part proportional to this scanning rate. However, in this case the power of resolution of the measurement is reduced due to the presence of the second term revealing the dynamic of the DSC. Again, the thermal time constant plays a key role at high scanning rates. It should be noted that the above equations are only valid for a large thermal diffusivity in the sample and the sample holder, so that the time constant of heat diffusion (τ_{int}) does not become the limiting factor. They are also valid under the assumption of perfect thermal symmetry of the calorimetric head (second order terms are not shown) [Claudy2005,Höhne2010]. Classical DSC based micro and nanotechnologies are rare. Let us mention SiN membrane DSC for heat capacity detection of nl-range liquid droplets [Youssef2009] and MEMS-DSC device where protein folding processes are analyzed via the measurement of differential heat capacity [Wang2008].

Fast Speed DSC:

In nanocalorimetry, the samples to be studied are so small that the internal thermalization time is not limiting. In this case, scientists have circumvent the problem of isolation of small samples in using scanning rates with values going from about 10^4 to 10^6 K/s. This new experimental technique, called “Fast Speed DSC”, has grown significantly in recent years. They use micro sensors, typically SiN thin membranes, produced through micro and nanotechnology [Minakov2005a),Herwaarden2005, Anahory2010]. These very high speeds yield to high sensitivities and allow measurements of very thin films from 100K to 1000K [Efremov2004,Lopeandia2008]. A last feature of these rapid calorimetric measurements is that at such high temperature rates, kinetics of studied thermal event can be observed. This is also true for high frequency nanocalorimetric methods as we shall see in the following.

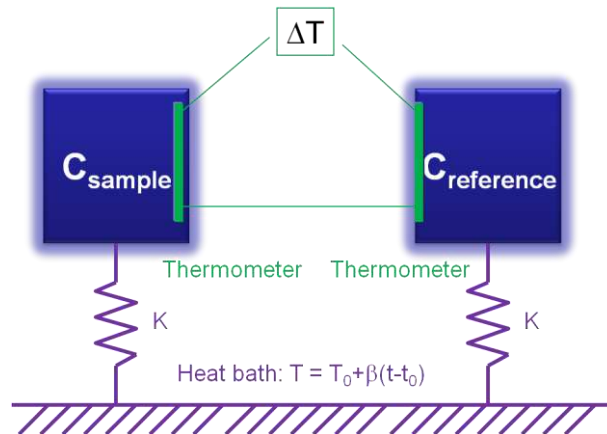


Figure 6 : Thermal scheme for DSC experiment. One cell contains the sample and the other cell contains a neutral reference. During the scanning temperature rate the temperature difference (or heat flux difference) is recorded as a function of time.

3.2.3 Isothermal calorimetry

A third widely used measurement method is called Isothermal Calorimetry [Ladbury1998]. It consists of measuring absorption (or removals) of energy in a sample over time at constant temperature (Figure 7). Titration nano-calorimetry is an experimental method issued from Isothermal Calorimetry in which

a compound A in solution (titrant) interacts with compound B in solution (titrate), producing or absorbing energy at constant temperature. If an aliquot (few percent in volume) of the titrant solution containing the molecule A interacts with the solution containing the molecule B, then the experiment can be carried out N times to achieve complete disappearance of B. In this way, through this type of experience, not only the enthalpy of reaction between molecules A and B can be obtained (during the firsts interactions), but also, thanks to the saturation curve $\Delta H = f(N)$, the constant of reaction between A and B is obtainable, like for acid-base chemical titrations. The constant of reaction allows access to the Gibbs free energy at a certain temperature. With calorimetric titration, we can access the thermodynamic parameters ΔH , ΔG and ΔS for the reaction A/B which provide complete thermodynamic data at determined temperatures. This technique is mainly used in chemistry, biochemistry and biology [Russel2006]. Since in this field, firstly biochemical and biophysical reactions generally have relatively low energy values, and secondly available volumes of biological samples are generally reduced (simply because they are expensive due to the cost of the synthesis) the use of nanocalorimetry is a natural choice. In past decades, the development of isothermal titration nanocalorimeters has been increasing a lot [Hakala2007,Xu2008]. Another approach to induce interaction of A with B is to mix the two solutions in the sensitive area via two differentiated liquid inputs. The mixture produces or absorbs energy in the sensitive area which is detected by the sensor and then flows through a third flow output path. One speaks about flow nanocalorimeters [Köhler1997,Zhang2004,Lerchner2008, Lee2009,Nam2010]. An original way of binding has been obtained by means of electrostatic mixing [Torres2008].

A major technical difficulty in the development of isothermal titration or flow nanocalorimeters is the need for a coupling of microfluidic techniques with that of the microfabrication of nanosensors. Indeed, one needs to bring the various liquid reactants on the measurement area while maintaining the highest thermal insulation of the same area. Certain isothermal nanocalorimeter measures only the power or heat released or absorbed by a small biological objects already positioned (e.g living cells) along time [Verhaegen2000,Johannessen2002,Chancellor2004]. In the field of biocalorimetry, volumes of analyzed samples are comprised between few nanoliter to few microliter, and minimum detectable powers are between few nanoWatt to few hundredth of nanoWatt depending on the nanocalorimeters designs. Integration of power measured versus time yields to minimum recorded energies from few tenth of nanoJoule to few microJoule (see tables showing performances of various isothermal calorimeters in reference [Lee2009] and [Braissant2010])

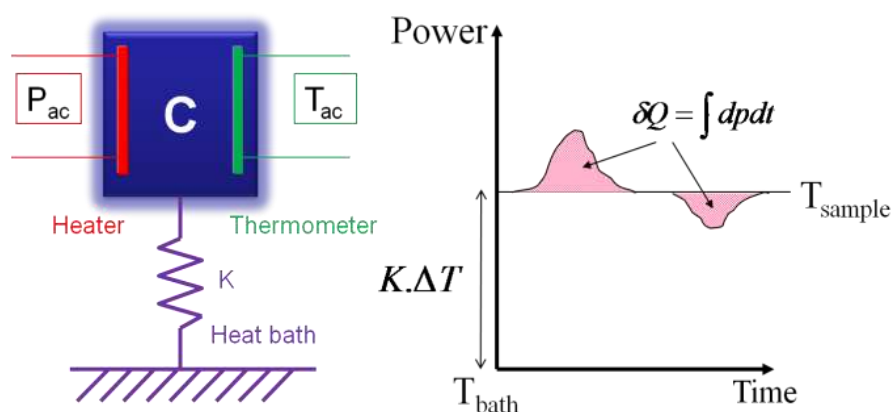


Figure 7 : Thermal scheme for isothermal calorimetry experiment. The power necessary to maintain the temperature of the sample at a constant value is represented versus time. The integration of this power provides the energy absorbed or dissipated by the sample at such temperature.

3.2.4 Low temperature calorimetry

Traditionally, at very low temperatures the most used calorimetric method is the adiabatic calorimetry. However, as the adiabatic nanocalorimetry is difficult to carry out at low dimension, scientists have developed new techniques known as dynamic calorimetry techniques, which overcome the problem of heat loss. There are two main different methods: the relaxation calorimetry and ac-calorimetry [Bourgeois2009]. Relaxation calorimetry overcomes poor insulation in directly measuring the exponential decay of the temperature of the sample compared to the thermal bath after a pulse of power. Measuring the thermal conductance K is necessary to have the heat capacity. On contrary, AC-calorimetry depends only on the frequency of temperature oscillations to be placed in adiabatic condition or quasi-adiabatic conditions. The sample temperature oscillates at a frequency such that no heat loss holds over one period of oscillation. In this case, it is not necessary to measure K . These different experimental techniques suitable for nanocalorimetry are described below.

Relaxation calorimetry. Relaxation calorimetry is to apply a heat pulse on the sensitive area of a sensor. An increase in the temperature of the sample appears; this increase will be faster than heat leak because the internal diffusion time is very short. The technique involves recording the decrease of the temperature sensor over time:

$$T = T_{bath} + \frac{P_0}{K} \exp\left(-\frac{t}{\tau}\right)$$

This decay is exponential and depends on the ratio between the heat capacity of the sensor with the sample and the thermal conductance to the bath. The thermal conductance can be estimated by other means, hence from the exponential decay the heat capacity can be deduced. This measurement is usually performed on a membrane where the thermometer and heater are lithographed. It is a sensitive method which may cover a large temperature range [Cooke2010]. One weak point of this technique is that the measure is not based on an oscillating method and therefore the SNR is degraded by the presence of thermal drift. This technique has been applied in some recent cases of specific heat measurement on very small sensors at low temperature [Suh2009, Chung2005].

AC calorimetry. In ac calorimetry an input thermal power $P(t) = P_{dc} + P_{ac}$ constituted by a dc and a ac term is supplied to a system connected to a thermal bath by means of a thermal conductance of known value [Corbino1910, Sullivan1968, Kraftmakher2002]. In focusing on the ac term only, the corresponding oscillating temperature T_{ac} is measured. At low frequencies the measurement is not adiabatic or quasi-adiabatic, and at high frequencies the temperature of the sample is not homogeneous anymore. This means that the thermal relaxation time and the thermal diffusion time have to be carefully taken into account. However, in choosing the appropriate frequency range, it is possible to circumvent the problem of thermal insulation of small objects to be measured by nanocalorimetry. It remains to design a calorimetric device with an appropriate working frequency range. The frequency of the temperature oscillation has to be faster than the relaxation time to the heat bath τ_{ext} (adiabatic condition) and slower than the diffusion time in the sensor τ_{int} . Under these circumstances, the heat capacity of the sample is simply obtained by the ratio of the ac power on the ac temperature:

$$C = \frac{P_{ac}}{i\omega T_{ac}}$$

The measured heat capacity is actually a complex number with real and imaginary components of different physical meaning. These are obtained by means of the measure of either the amplitude or the phase of the oscillating temperature. This method is particularly sensitive because locking-amplifiers with narrow bandwidth filter can be used for oscillating temperature recording but also because dc or low frequency thermal drifts are less important. Heat capacity resolutions $\Delta C/C$ of the order of 10^{-5} to

10^{-4} are currently obtained while in relaxation calorimetry or other methods resolutions lay between 10^{-3} to 10^{-2} . Thus, ac-calorimetry is a technique particularly adapted to nanocalorimetry because, on one side it allows measures on small objects, and on another side it allows measurement in the nanoJoule/Kelvin or nanoJoule/picoJoule ranges [Fominaya1997,Lopeandia2010]. Although ac calorimetry has been developed in the field of low temperature physics [Minakov2005b)], for few decades it has been adapted to different temperature ranges in several domains of research (magnetic films, biological objects, polymers, etc...) where the detection of fine phase transitions or phase transformations were researched [Yao2003,Garden2004,Garden2009]. More precisely, the record in sensitivity was obtained in attojoule calorimetry (10^{-18} Joule) which allowed access to complete new physics [Bourgeois2005]. The principal inconvenient of ac calorimetry is the useable frequency range limited to no more than one or two decades when measurement of the dynamic of the studied system via $C(\omega)$ is wanted. This disadvantage is avoided in another dynamic calorimetric method called 3ω method.

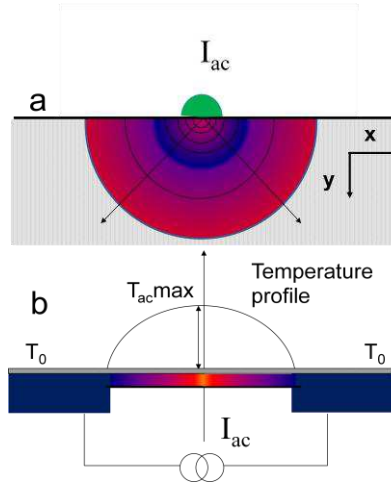


Figure 8 Schemes of the 3ω method with the thermal wave in the plane (perpendicular to the transducer) (a) or along the sample (parallel to the transducer) (b).

3.2.5 Other methods

3ω -method. In the 3ω method, the thermal power that generates temperature oscillations in the sample is provided by the thermometer itself. A current of frequency f passes through the thermometer-like-heater resistance (called the transducer) which produces a thermal power oscillating at frequency $2f$ due to Joule effect. As the transducer temperature varies at that frequency, this results in a $3f$ term which contains all the thermal information of the sample [Corbino1911,Birge1997]:

$$\delta T_{ac} = \frac{P_0}{K\sqrt{1+(\omega\tau)^2}} \text{ or } \delta T_{ac} = \frac{P_0}{\sqrt{2\omega CK}}$$

The two above equations apply depending on the geometrical design of the sensor. ω is the pulsation, related to the frequency through $\omega = 2\pi f$. At very low frequency the amplitude of the temperature oscillation is only related to the thermal conductance. If the measurement is made as a function of the frequency, the heat capacity can be extracted through the estimation of the thermalization time $\tau = C/K$.

The purely electrical term oscillating at frequency f , which is much larger than the $3f$ component, has generally to be removed using a Wheatstone bridge circuit, otherwise the quality of the measurement will suffer. This method, non-adiabatic by principle, was used to measure the thermal properties of material of very small thermal diffusivity for which a frequency dependence of the specific heat was

expected. It has for example been successfully used to study the frequency dependent specific heat at the glass transition of some glass-formers over several decades of frequency [Birge1997]. Depending on the geometry of the couple transducer with sample, the thermal effusivity $c \times k$ (product of specific heat by thermal conductivity) is measured or, upon particular geometrical conditions, the thermal conductivity k is directly measured at low-frequency (see equations above) [Cahill1990]. In nanocalorimetry, this method has been successfully applied to the measurement of the thermal conductivity of crystalline silicon wires of nanometric sizes for which phonon-blocking effects were observed at very low temperatures [Bourgeois2007,Heron2010]. Recent experiments use the 3ω method for thermal properties measurement of nl liquid-like samples [Choi2008,Park2010].

Unconventional methods: measurement of caloric curve. In this technique developed for the in flight measurement of clusters (hundred of atom), one use the photofragmentation of the clusters by a laser beam to estimate the internal energy U as a function of temperature. The clusters ions are selected using a mass spectrometer and thermalized in helium gas. Then they are irradiated by a laser, the fragments produced are analysed by a second mass spectrometer. Their number depends directly on the inner energy of each clusters, hence its measurement gives the internal energy of the cluster. Its derivative ($C = \frac{\partial U}{\partial T}$) will give the heat capacity of the clusters ions (see references [Schmidt1997,Breaux2003]). Melting point and heat capacity of cluster of 140 atoms or less could be measured using this technique a performance never equaled with other technique. Others unconventional methods of nano and microcalorimetry exist but are not described in this brief essay.

4 Micro and Nanosensors

It is the need of doing thermodynamic measurements on specific physical or chemical nanosystem that will determine what type of sensor that must be developed for nanocalorimetry. Secondly, the choice of the experimental technique (as detailed in the previous section) will also influence the conception of the sensing part. Several examples of nanocalorimeter based on micro or nanofabrication are shown below where the best results have been obtained in terms of sensitivity and/or resolution. Great care must be taken in the choice of materials along with the geometry of the system (thermometry and heater); it will fully determine the thermal performance of the sensor. Two main parameters should orient the choice of materials for the sample holder: small heat capacity and a complete absence of phase change in the working temperature area to avoid spurious signal coming from the holder. The geometry will be chosen to reduce the leak to the heat bath or to control it through a dedicated thermal link. Thermal data of the main materials used for manufacturing sensors are summarized in Table 1. This table will be fruitfully used during the design of a new sensor depending of its future working temperature range or its particular specifications (materials compatibility).

The first attempt to measure the heat capacity of thin films was done by G.D. Zally et al [Zally1971]. He built a calorimeter based on a very thin pyrex membrane where thermometer and heater were attached. Since this attempt, numerous different sensors have been built in various materials from silicon, silicon nitride, glass to polymer. We will detail below some of them.

Table 1 Thermal parameters for various materials from high temperature to very low temperature. The thermal conductivity is given in W/cmK and the specific heat in J/gK.

	Si		SiN		Pur copper		Polymer (PTFE)		Glass	
	c	k	c	k	c	k	c	k	c	k
1000K	8.2	0.3	4	0.2	0.5	4	NA	NA	3	$2 \cdot 10^{-2}$
300K	6.7	1.5	2	0.1	0.3	4	0.9	$3 \cdot 10^{-3}$	1	10^{-2}
100K	2.5	8	1	$4 \cdot 10^{-2}$	0.25	5	0.3	$2 \cdot 10^{-3}$	0.6	$8 \cdot 10^{-3}$
10K	$2 \cdot 10^{-3}$	0.3	10^{-3}	$6 \cdot 10^{-3}$	$8 \cdot 10^{-4}$	160	0.18	10^{-3}	$6 \cdot 10^{-3}$	10^{-3}

1K 0.1K	5.10^{-7}	$\sim 10^{-3}$	$\sim 10^{-6}$	5.10^{-4}	$\sim 10^{-5}$	40	$\sim 10^{-3}$	7.10^{-5}	7.10^{-6}	5.10^{-4}
	$\sim 10^{-11}$	NA	$\sim 10^{-9}$	NA	$\sim 10^{-6}$	0.4	NA	NA	8.10^{-8}	10^{-5}

4.1 Silicon, silicon nitride or diamond membranes

As mentioned above, the choice of the materials is given by the specification of the experiment to be performed. The best material for application in a wide temperature range (from 40K to 1000K) is, for sure, silicon nitride (SiN). This amorphous material is totally inert in that temperature window and can be easily manipulated. Fabrication of membrane out of SiN is masterized in all clean room in the world using chemical etching of silicon by KOH (see the sketch in fig. 9). Thermometer and heater can be lithographed on top which permits the measurement of thermal properties. The design of the heat link and the choice of materials for the transducers will set the performance of the calorimeter.

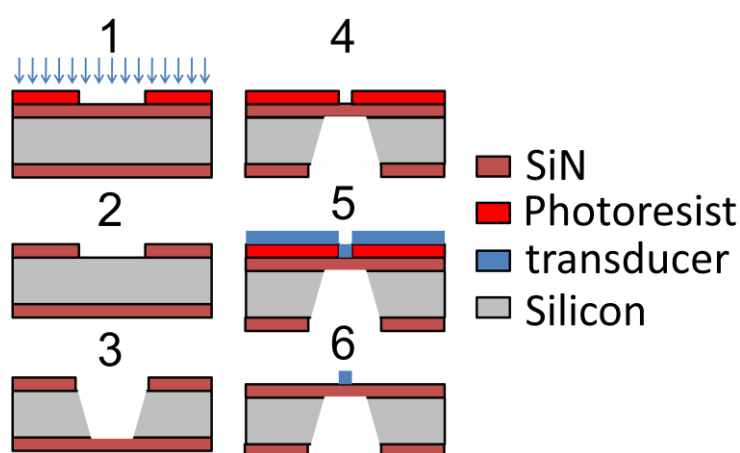


Figure 9 Example of microfabrication procedure of a suspended membrane of SiN. 1-Spinning of resist and photolithography, 2-Remove the resist 3-chemical etching of silicon with KOH, 4-Photolithography of the transducer 5-deposition of the transducer 6-lift-off.

If one wants to applied nanocalorimetry technique at low or very low temperature SiN is not the best choice. As it can be seen in the table 1, the heat capacity is high as compared to single crystal silicon. Then the fabrication of silicon membrane is more appropriate and should be preferred. Moreover, the structuring of the membrane will be absolutely necessary to create a well defined isotherm. Indeed, the thermal conductance of silicon (or SiN) is still high below 10K and then a proper thermal isolation lies in suspending a membrane through isolated arms (see Fig. 2a or b). On the figure 10, examples c), g) and i) are silicon membrane for isothermal flow-through or small-volume-liquid nanocalorimetric measurements.

4.2 Polymer membranes

In nanocalorimetry, thin polymer membranes are also used to insure good thermal insulation of the measurement area. This type of membrane is mostly used for medium to high temperatures because of the low thermal conductivity of polymers (see table 1). At very low temperatures, they are less attractive because their heat capacity is very high (see table 1). To ensure uniformity of temperature in these sensors, the low thermal diffusivity of these materials is generally eliminated through the deposition of a thin layer of metal diffusing heat over the entire surface of the sensitive area (eg gold, aluminum, silver, ...). Figures 2 d) and f) and figure 10 a), d) and h) are examples of polymer membranes for experiments of ac-nanocalorimetry or isothermal nanocalorimetry on thin magnetic films, thin polymer films and low volumes chemical or biological objects or reactions. The thickness

of these membranes can range from a few hundreds of nanometers to several tens of micrometers. The use of micro and nano technologies is obviously necessary to deposit and lithographically machined sensing elements on the membrane, as well as a possible step of membrane design through dry etching techniques (reactive ion etching or oxygen plasma for example).

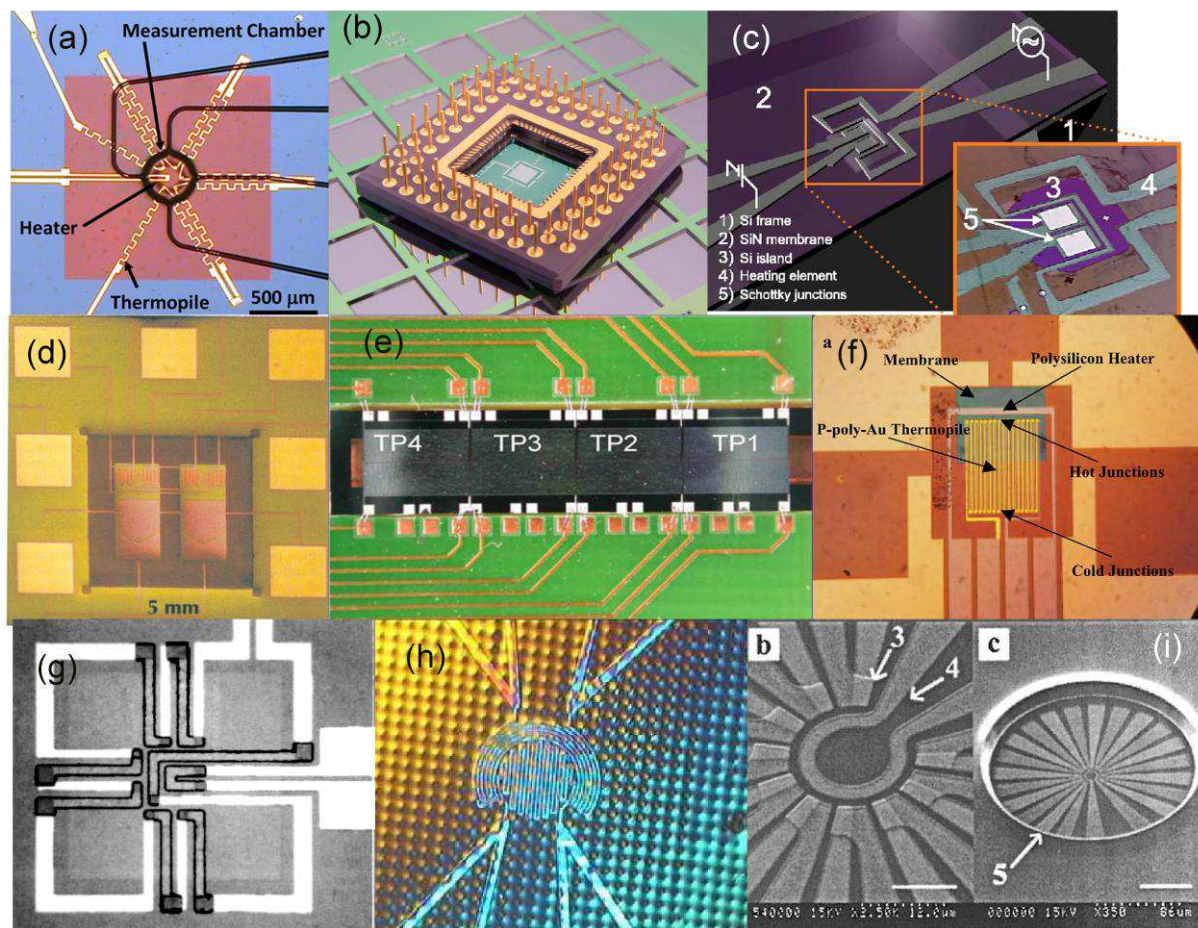


Figure 10 : Various sensors for isothermal or biological liquid-sample nanocalorimetric experiments. a) Parylene membrane for isothermal chemical and biological interactions [Lee2009], b) silicon sensor for isothermal chemical and biological interactions 'Photograph courtesy www.xensor.nl' [Herwaarden2005], c) Silicon nitride sensor for small-volume-liquid calorimetric detection [Hakala2007], d) Polyimide membrane for electrostatic-liquid-mixing calorimetric detection [Torres2008], e) Silicon microfluidic chamber for flow-through isothermal calorimetry [Lerchner2006], f) glass microfluidic reaction chamber for flow-through calorimetry [Zhang2004], g) Silicon nitride membrane for small-volume-liquid calorimetric detection [Chancellor2004], h) micro-posts sustained polyimide membrane for small-volume-liquid calorimetric detection [Garden 2009], i) Silicon nitride suspended sensor for isothermal detection of living cells [Johannessen2002].

5. Conclusion

In that not complete review, various experimental methods named “nanocalorimetry” have been presented. It has been shown that it concerns all calorimetric method for which the dimensions of the objects studied are in the order of magnitude of nanometer, or measured energy or power are in the range of nanojoule or nanowatt. The review has been based on numerous examples of nanocalorimeters existing in the literature from low temperature to room temperature with application in condensed matter, chemistry, biophysics or biology in general. The aspect of micro and nanofabrication essential for the achievement of nanocalorimetric devices has been emphasized as

well as the importance of sensitive instrumentation, electronic conditioning, and the choice of materials for the thermal detectors.

Calorimetry is by essence a universal method of measurement covering by this way a wide spectrum of different researches. The emergence of nanocalorimetry in recent decades has allowed the exploration of new and original fields of research. With the evolution of modern micro and nanofabrication technologies many new developments will appear especially towards more sensitive sensor especially in biophysics. Significant room for improvement still exists in many areas of nanoscience which makes nanocalorimetry a quite open subject of research.

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